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WORKS ON THERMOMETRY OF LOW TEMPERATURES IN USSR

P. G. Strelkov

/A Digest/

The subject of this article, which was read 9 November 1949 at a seminar of the Institute of Physical Problems, Academy of Sciences USSR, is the measurement of temperatures not lower than those obtained with the aid of liquid hydrogen, i.e., between room temperature and -259°C. It is mainly of interest for chemical thermodynamics, since the third law of thermodynamics enables one directly to employ low temperatures in organic chemistry, which could use the absolute values of entropy of important compounds that would be obtained from low-temperature measurements; these entropy values are needed to obtain the thermodynamic criterion governing the possibility of any reaction or to calculate equilibrium constants. Therefore, entropy must be determined systematically under standard conditions.

To do this one must be able to measure temperatures down to -259°C; lower temperatures need not be measured since extrapolation or the cubic law can give sufficient accuracy for most practical cases involving temperatures below 14 or 10° K.

Entropy is usually obtained by graphic integration. If phase transitions happen in the limits of integration, the sections between them are integrated and to the sum are added the variations in entropy which are caused by the transitions; to determine these entropy values it is necessary to have a procedure for measuring the temperature and the heats of transformation, melting, and evaporation. Obviously, one must be able to measure the thermal capacity in the gaseous and condensed states.

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All these measurements require accurate determination of temperature and especially temperature differences. The first steps toward this goal were, of necessity, works on the obtaining and measuring of temperatures down to about 260°.

This work was begun in 1940 at the Institute of Physical Problems, where refrigeration equipment insured the necessary coldness.

The Moscow Institute of Measurements and Measuring Instruments (MGIMIP) took part from the very beginning. In fall 1948 a low-temperature laboratory was organized in the MGIMIP.

At the end of 1949 a plant for the liquefaction of hydrogen was put into operation at the MGIMIP, with a productivity of about 1.5 liters of liquid per hour. The plant employs the Joule-Thomson effect and is served by compressors made by the Experimental Factory of the Petroleum Institute, Academy of Sciences USSR. Thus, another low-temperature laboratory arose, in which measurements of heat capacity were organized.

Work on thermometry was begun in 1940 on the lower part of the international scale which accurately reproduces the thermodynamic scale from 0 to 660° C and from 0 to -190° C.

To reproduce the international scale down to -190° C, it was necessary to have an excellent platinum resistance-thermometer and instruments for measuring its resistance at the four datum marks which are the temperatures of the phase equilibria: liquid-vapor of sulfur (444.60° C), liquid-vapor of water, liquid-solid phase of water, and liquid-vapor of oxygen (-182.97° C).

In 1940 the meteorological laboratories did not certify the beta coefficient in platinum thermometers; therefore, procedures had to be worked out for reproducing the boiling point of oxygen and constructing resistance thermometers to be used at such low temperatures. This work was completed by P. G. Strelkov and V. I. Lin'kov. An original model of a platinum thermometer on a helicoidal quartz body was the main feature of this work; it has been introduced into practice.

This thermometer was of small dimensions and gave fine stability of readings and very small inertia; it was considerably better than the German ones used earlier.

During the first years of the war, the work turned to the calculation of tables that permit accurate determination of temperatures (0 to -190° C) measured on any platinum thermometer, with the introduction of corrections that take into consideration the various coefficients delta and beta of different thermometers. The tables saved the time consumed in calculating temperatures by successive approximations; the fourth-power formula of the international scale was used.

In 1945, 18 platinum thermometers with helicoidal body were constructed by N. A. Brilliantov, V. I. Lin'kov, and the author. Their accuracy corresponded to $R_{100}/R_0 = 1.3924$, thanks to the cooperation of the Institute of General Inorganic Chemistry, Academy of Sciences USSR. The platinum was refined by a method proposed by I. I. Chernyayev and A. M. Rubinshteyn; its purity was found to be 99.9998% by the author using spectral analysis.

In 1947, A. S. Borovik-Romanov and P. G. Strelkov constructed a gas thermometer of constant density in the IFP and worked with it in 1948 at the MGIMIP.

As a result of new work in 1948 on a relative scale involving a comparison of groups of thermometers, the temperature of the ternary point of oxygen was determined as $54.37 \pm 0.03^\circ$ K.

In 1949, M. P. Orlova constructed an apparatus for determining the boiling temperature of a liquid oxgyen bath, convenient for reproducing the datum mark on the international scale. Also in 1949, A. S. Borovik-Romanov measured the temperature behavior of saturated vapors of parahydrogen, thus guaranteeing a region below 20° K.

Several temperatures of phase equilibria, and thus several other datum marks, must still be measured. M. P. Orlova has constructed a calorimeter which will be used in 1950 in new measurements of heat capacity. At present, temperatures can be measured down to -259° C with an accuracy of about 0.1°.

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